Structure and thermoelectric properties of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ samples prepared by HPHT

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Abstract: Double-filled CoSb_3 is one kind of the most promising thermoelectric materials, the choice and concentration of filled atoms are the key for the high figure of merit values (ZTs). We report the transport properties of In and Ba filled skutterudite prepared by a high-pressure synthesis approach, the processing time was sharply reduced from a few days to half an hour. The main parameters, including Seebeck coefficient, electrical resistivity and thermal conductivity, were all investigated in the temperature range of 323-723 K. $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ showed a relatively good ZT value attributed to both the enhanced power factor and the low thermal conductivity. And the multiple microstructures, defects and strains were also revealed by high-resolution transmission electron microscopy (HRTEM) images.

Keywords: Skutterudite; Thermoelectric properties; HPHT; Seebeck coefficient

1. Introduction

A large number of researches have focused on thermoelectric technology for nearly three decades due to the increasing demand of energy and the desire for improved efficiency [1-5]. The coefficient of performance for a thermoelectric cooler or the conversion efficiency of a thermoelectric generator depend on the dimensionless figure of merit, which is defined as $ZT = \alpha^2 \sigma T / \kappa$ [6-11], where α is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity and T is the temperature in Kelvin. Generally, κ is the sum of electronic thermal conductivity κ_e and the lattice thermal conductivity κ_{ph} .

CoSb_3 materials are considered as one of the most promising middle temperature thermoelectric materials for automotive thermoelectric waste heat recovery, due to their small band gap, high carrier mobility and modest thermopower. Although CoSb_3 materials have many advantages, high thermal conductivity is still hindering its

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application. Therefore, a great deal of research has focused on how to reduce the thermal conductivity [12, 13]. Many studies [14-18] showed that the high thermal conductivity in the binary CoSb_3 can be reduced significantly by introducing single, double and multiple filler atoms. As compared to the pure CoSb_3 materials, these filled skutterudites have a much lower lattice thermal conductivity is mainly due to the incoherent rattling of the weakly bound filling atoms in the structure and the scattering of acoustic phonons for resonant interaction between guest atoms and lattice phonons in filled skutterudites.

Many studies have shown that ZT values of thermoelectric materials can be improved extraordinarily at high pressure. Unfortunately, the perfect performance under high pressure immediately reverted back to the primitive state when the pressure is reduced to normal pressure. Zhang et al.[19] reported they have prepared Li-filled CoSb_3 materials successfully using high pressure synthesis method, it is worth noting that Li cannot be filled normally. The high pressure and high temperature (HPHT) synthesis method can not only increase the filling ratio of atoms and broaden the filling type of elements, but also optimize the thermoelectric properties of materials effectively. In this study, In and Ba double-filled skutterudite bulk materials with different nominal composition $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ ($x+y=0.5$) were prepared by the HPHT method for only half an hour. The effect of the In and Ba filling fraction on the thermoelectric properties of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ and the microstructure induced by high pressure will be reported in this paper.

2. Experimental procedure

The nominal chemical ratio $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ ($x+y=0.5$) samples were prepared by indium, barium, antimony and cobalt (99.9% in purity) powders as sources. The mixed powder was milled in argon as the protective gas, and then which were compressed into a thick 3 cm and diameter of 10 cm cylindrical sample by Hydraulic press. After that, the samples were prepared by a cubic anvil high pressure apparatus (SPD 6×1200 made in China) at about 900 K and the synthesized pressure was 1GPa. The crystal phases of the synthesized samples were characterized using a Rigaku D/max-2500 X-ray powder diffractometer (XRD) with Cu Ka radiation in the range of 20 to 80 degrees. The morphology of the fractured surface and the investigation of microstructures were observed by field emission scanning electron microscopy (SEM JEOL JSM-6700F) and HRTEM (JEOL JEM-2200FS). The carriers concentration and carrier mobility at room temperature were measured by (HMS 3000). The Seebeck

coefficient (S) and electrical resistivity (ρ) were measured simultaneously by the ZEM-3 commercial equipment (Ulvac-Riko) in the temperature range of 323-723 K. The thermal diffusivity was measured on a laser flash thermal constants measuring with the commercial system (Netzsch LFA 427) apparatus in temperature range of 323-723 K.

3. Results and discussion

X-ray diffraction (XRD) patterns of bulks with different In and Ba contents are shown in Fig. 1. For $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ sample, except for impurity phase InSb, all of the diffraction peak positions and (hkl) values match very well with the standard diffraction data of pure CoSb_3 . For $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$ sample, the XRD peaks of impurity slightly deviated from the standard XRD patterns of Ba_2Sb_3 (PDF No.78-230), which is caused by the fact that excess barium.

Fig. 1 XRD patterns of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ samples prepared by HPHT.

Fig. 2a and 2b show the SEM micrographs for the fractured surfaces of $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$ and $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$, respectively. The samples have abundant boundaries and a wide crystal size distribution ranging from nano-particles to 5 μm . A large number of **secondary phases** can be found in Fig. 2a, the enlarged image of area 1 has been pointed out by arrow. According to the results of EDS and XRD test, the **secondary phases are barium compound. So, the actual filling fraction of Ba for $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$ sample derived from EDS is less than the nominal compositions.** From Fig. 2b we can see that a large number of nano-particles with the size of ranging from 50-200 nm can be found sticking to the grain boundaries. It is possible that the grains of different sizes have different chemical compositions. In order to further find out the difference between the five areas, the chemical composition of different regions (1, 2, 3, 4, 5) has been measured. For areas 1 and 2(Fig. 2b), the content of Ba

is much higher than that of area 3, 4 and 5 (Fig. 2b).

Fig. 2d and 2e show numerous nanodots and dislocations et al embedded in the matrix for sample $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$. It can be seen that lattice deformation obviously exists in the lattice, as marked in Fig. 2d (see white hexagon area). Many fringes belong to stacking disorder also can be found in Fig. 2d (see white circle area), which are resulted by the twist and relative shift of the overlapped planes by high pressure stress. In addition to the above, nano-sized incoherent precipitates (nanodots) with slightly different crystalline orientations and lattice distances within the matrix grains are observed by HRTEM, as shown in Fig. 2e (see white square marking). To show the defect of Fig. 2e more clearly, the inverse fast Fourier transform (IFFT) image (Fig. 2f) has been used. The IFFT clearly shows that a small stacking disorder appeared on the basal plane, which could be explained by the local shift of atoms caused by the exact lattice points. **The different kinds of defects would scatter phonons more effectively and further decrease the thermal conductivity of the bulk material.**

Fig. 2 SEM micrographs of $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$ (a) and $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ (b), EDS results of the selected areas (c). Typical HRTEM images of $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ sample (d) lattice deformation, (e) the possible “nanodots” and (f) IFFT image corresponding to (e).

Table 1. the carrier concentration and carrier mobility of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ at room temperature.

	$\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$	$\text{In}_{0.25}\text{Ba}_{0.25}\text{Co}_4\text{Sb}_{12}$	$\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$
carrier concentration (10^{19} cm^{-3})	-3.12	-5.16	-8.37
carrier mobility ($\text{cm}^2\text{V}^{-1} \text{ s}^{-1}$)	90.75	71.2	58.1

The temperature dependence of electrical conductivity for $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ is shown in Fig. 3a. The electrical resistivity decreases greatly with the content of In filling. Besides $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$ sample, the electrical resistivity of other samples all increase with increasing temperature, indicatives of degenerate semiconductor character. We can also note that, these compounds all possess a minimum value of electrical resistivity at 323 K, and the minimum value (1.2 mΩcm) of $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ is obtained. But the electrical resistivity of $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$ sample is relatively higher than that of single Ba filling [11].

The temperature dependence of Seebeck coefficients for $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ is shown in Fig. 3b. All samples reveal typical n-type transport behavior as they have negative α . The absolute Seebeck coefficients decrease with the content of In filling in the temperature range of 323-600 K. The decrease in electrical resistivity and absolute Seebeck coefficients of samples $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ with the increase of In filling are mainly due to the reduction of the carrier concentration induced by the In filler. The absolute Seebeck coefficients of $\text{In}_{0.25}\text{Ba}_{0.25}\text{Co}_4\text{Sb}_{12}$ and $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$, which increase with the increasing temperature, all show their maximum values at 623K. The increase of Seebeck coefficients is presumed to be due to the increasing number of thermally excited minority carriers at higher temperatures which tend to decrease the Seebeck coefficients.[20]

Fig. 3c shows the temperature dependence of the power factor (PF), which was calculated from the measured absolute Seebeck coefficient α and the electrical resistivity ρ according to the following formula: $\text{PF}=\alpha^2/\rho$. As expected from the results of the effect for ρ (Fig. 3a) and α (Fig. 3b), the power factor value increases with the content of In filling. The PF value of sample $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ gradually increases with increasing temperature and shows its maximum value ($29.7 \mu\text{Wcm}^{-1}\text{K}^{-2}$)

at about 623 K, and then it begin to decrease.

Fig. 3 temperature dependence of (a) electrical resistivity, (b) Seebeck coefficients and (c) power factors of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$

The temperature dependence of thermal conductivity for $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ is shown in Fig. 4a. The figure shows that the thermal conductivity of samples all decrease with the increasing temperature, and the trend of decline slow down at higher temperature. The thermal conductivity of $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ and $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$ are significantly lower than that of $\text{In}_{0.25}\text{Ba}_{0.25}\text{Co}_4\text{Sb}_{12}$, and the thermal conductivity of $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ showed the lowest value of $2.16 \text{ Wm}^{-1}\text{K}^{-1}$ at 723 K.

As a part of thermal conductivity, the lattice thermal conductivity κ_{ph} change tendency is shown in Fig. 4b. Electronic thermal conductivity κ_{e} , which is another part of the thermal conductivity, is calculated by the Wiedemann–Franz's law $\kappa_{\text{ph}} = L\sigma T$ with the Lorenz number $L = 2.0 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ [21], in which σ refers to electrical conductivity and T refers to the absolute temperature. The lattice thermal conductivity can be obtained by subtracting the electronic component from total thermal conductivity ($\kappa_{\text{ph}} = \kappa - \kappa_{\text{e}}$). The relationship between lattice thermal conductivity and temperature is the same as thermal conductivity (Figure. 4a). The lowest κ_{ph} of $1.31 \text{ Wm}^{-1}\text{K}^{-1}$ has been obtained for sample $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$, comparable with other element filled CoSb_3 samples at similar filling fraction [18, 22]. There are two main reasons for such low thermal conductivity: the first factor is related to the phonons scattered by the filler atoms provided by In and Ba; the second factor is the enhancement of point defect scattering and the disorder among the lattices by HPHT synthesis method.[23]

Fig. 4 variations in (a) thermal conductivity and (b) lattice thermal conductivity for $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ as a function of temperature

According to the measured Seebeck coefficient, electrical resistivity and thermal conductivity, the figure of merit ZT values are calculated and shown in Fig. 5. The ZT values of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ samples all increase with the increasing of temperature. The ZT value of sample $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ is significantly higher than that of other samples, and the maximum value (0.97) is obtained at 723 K. This mainly benefits from the distinct decrease in electrical resistivity and thermal conductivity.

Fig. 5 Temperature dependence of thermoelectric figure of merit (ZT) for

$\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ prepared by HPHT.

4. Conclusion

Double-filled skutterudite $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ ($x+y=0.5$) samples have been synthesized by the HPHT method. With the increase of In filling ratio, the electrical transport properties of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ samples were optimized obviously. The thermal transport

properties can be improved significantly by changing the ratio of In and Ba filling, and some microstructures due to high pressure have been partially kept to ambient pressure. $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ sample showed a very low thermal conductivity, and the maximum ZT value of 0.97 has been obtained for an In and Ba double-filled sample at 723 K.

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Illustration of figures:

Fig. 1 XRD patterns of the samples of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ prepared by HPHT.

Fig. 2 SEM micrographs of $\text{In}_{0.05}\text{Ba}_{0.45}\text{Co}_4\text{Sb}_{12}$ (a) and $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ (b), EDS results of the selected areas (c). Typical HRTEM images of $\text{In}_{0.4}\text{Ba}_{0.1}\text{Co}_4\text{Sb}_{12}$ sample (d) lattice deformation, (e) the possible “nanodots” and (f) IFFT image corresponding to (e).

Fig. 3 temperature dependence of (a) electrical resistivity, (b) Seebeck coefficients and (c) power factors of $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$.

Fig. 4 Variations in (a) thermal conductivity and (b) lattice thermal conductivity for $\text{In}_x\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ as a function of temperature.

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